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(54) **Highly active double metal cyanide complex catalysts**

Hochwirksame Doppelmetallcyanidkatalysatorenkomplex

Catalyseurs à base de complexe de cyanure de deux métaux hautement actifs

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Description

FIELD OF THE INVENTION

[0001] The invention relates to double metal cyanide (DMC) complex catalysts useful for epoxide polymerization. The catalysts, which contain an unusually low level of metal salt, are highly active. The invention includes methods for preparing the catalysts. Polyether polyol products made using the catalysts have exceptionally low unsaturations.

BACKGROUND OF THE INVENTION

[0002] Double metal cyanide (DMC) compounds are well known catalysts for epoxide polymerization. The catalysts are highly active, and give polyether polyols that have low unsaturation compared with similar polyols made using basic (KOH) catalysis. Conventional DMC catalysts are prepared by reacting aqueous solutions of metal salts and metal cyanide salts to form a precipitate of the DMC compound. The catalysts can be used to make a variety of polymer products, including polyether, polyester, and polyetherester polyols. Many of the polyols are useful in various polyurethane coatings, elastomers, sealants, foams, and adhesives.

[0003] DMC catalysts are usually prepared in the presence of a low molecular weight organic complexing agent, typically an ether such as glyme (dimethoxyethane) or diglyme. The complexing agent favorably impacts the activity of the catalyst for epoxide polymerization. Other known complexing agents include alcohols, ketones, esters, amides, ureas, and the like. Recently, we described substantially amorphous DMC catalysts prepared using water-soluble aliphatic alcohol complexing agents such as tert-butyl alcohol (EP-A-0654302). In one conventional preparation, aqueous solutions of zinc chloride and potassium hexacyanocobaltate are combined. The resulting precipitate of zinc hexacyanocobaltate is combined with an organic complexing agent. The resulting catalyst has the general formula:

$$Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yH_2O \cdot z\text{Complexing agent}$$

[0004] DMC catalysts are made with an excess of the metal salt compared with the amount of metal cyanide salt used. See, e.g., U.S. Pat. Nos. 3,427,256, 3,278,457, and 3,941,849. More recently, we taught (U. S. Pat. No. 5,158,922) an improved process for making easily filtered DMC catalysts by controlling the order of reagent addition, the reaction temperature, and the stoichiometric ratio of the reactants. The '922 patent teaches to use at least about a 100% stoichiometric excess of the metal salt relative to the metal cyanide salt. Thus, in the example above, at least about 3 moles of zinc chloride is used per mole of potassium hexacyanocobaltate. The examples in the reference use glyme as the organic complexing agent. Zinc hexacyanocobaltate catalysts prepared by this procedure generally have zinc chloride to zinc hexacyanocobaltate mole ratios of about 0.6 or more. The '922 patent discloses (in a formula) compositions having as little as 0.2 moles of metal salt per mole of DMC compound in the catalyst.

[0005] While the procedure described in the '922 patent (large excess of zinc chloride) works well with glyme, it is less satisfactory for use with other complexing agents, including tert-butyl alcohol. When tert-butyl alcohol is used, the catalyst precipitate becomes gelatinous and difficult to isolate. In addition, the activity of these catalysts for epoxide polymerizations, although quite high compared with KOH catalysts, is still somewhat less than desirable. The catalysts prepared by the reference procedure with glyme as the organic complexing agent typically polymerize propylene oxide with an activity less than about 2 g PO/min at 100 ppm of catalyst, based on the weight of finished polyol, at 105°C.

[0006] Recently, we described substantially amorphous DMC catalysts (EP-A-0654302). These catalysts are preferably made using a water-soluble aliphatic alcohol complexing agent such as tert-butyl alcohol. An excess amount of metal salt is used to make the catalyst. Zinc hexacyanocobaltate catalysts described therein have more than 0.2 moles of metal salt per mole of zinc hexacyanocobaltate present, typically more than 0.5 moles of metal salt per mole of zinc hexacyanocobaltate. The X-ray diffraction patterns show that the catalysts are substantially amorphous; i.e., the catalysts are characterized by the substantial absence of sharp lines in the powder X-ray diffraction pattern (see Fig. 5). The catalysts described in the '534 application have far greater activity for polymerizing propylene oxide than previously known catalysts. For example, rates in excess of about 3 g PO/min at 100 ppm of catalyst were achieved.

[0007] Improved double metal cyanide catalysts are needed. Preferred catalysts would be easy to prepare and isolate, and would have excellent activity for polymerizing epoxides. Preferred catalysts would give polyether polyols having narrow molecular weight distributions and low unsaturation.

SUMMARY OF THE INVENTION

[0008] The invention is an improved catalyst for polymerizing epoxides. The catalyst is a double metal cyanide (DMC) complex crystalline catalyst which comprises a DMC compound, an organic complexing agent which is a water-soluble aliphatic alcohol, and a metal salt, wherein the catalyst contains less than 0.1 mole of the metal salt per mole of DMC compound. Like other DMC catalysts, these complexes are made by reacting aqueous solutions of a metal salt and a metal cyanide salt in the presence of an organic complexing agent. The metal salt is used in excess compared with the amount

of metal cyanide salt, and the resulting DMC complex includes some of the metal salt. Unlike previously known catalysts, these catalysts contain less than 0.1 moles of the metal salt per mole of DMC compound in the catalyst.

[0009] In contrast to the substantially amorphous DMC catalysts that we discovered previously (EP-A-0654302), the catalysts of this invention exhibit a powder X-ray diffraction pattern of sharp lines (see Figs. 2 and 3). Surprisingly, these crystalline catalysts have excellent activity for polymerizing epoxides (greater than 3 g PO/min at 100 ppm catalyst). The catalyst activities are significantly higher than the activities available from conventional KOH catalysts, and are also higher than those of ordinary DMC catalysts (as reported, e.g., in U. S. Pat. No. 5,158,922). Previously, the only catalysts known to have such high activities were the substantially amorphous catalysts described in EP-A-0654302. Polyols made using the catalysts of the invention have exceptionally low unsaturation, typically less than 0.006 meq/g.

[0010] The invention also includes methods for making the catalysts of the invention. In accordance with one aspect of the invention, there is provided a method of making a highly active DMC complex crystalline catalyst according to Claim 1, said method comprising reacting aqueous solutions of a metal salt and a metal cyanide salt in the presence of an organic complexing agent, wherein the metal salt is used in an excess amount less than a 100% stoichiometric excess relative to the amount of metal cyanide salt, and the resulting catalyst contains less than 0.1 mole of the metal salt per mole of DMC compound in the catalyst. In accordance with a further aspect of the invention, there is provided a method of making a highly active DMC complex crystalline catalyst according to Claim 1, said method comprising:

(a) reacting aqueous solutions of a metal salt and a metal cyanide salt in the presence of an organic complexing agent to produce a catalyst precipitate said metal salt being used in excess compared with the amount of metal cyanide salt used; and
(b) washing the catalyst precipitate with a mixture of water and organic complexing agent in a manner effective to produce a highly active DMC complex catalyst that contains less than 0.1 mole fo the metal salt per mole of DMC compound in the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 shows a plot of propylene oxide consumption versus time during a polymerization reaction with one of the catalyst compositions of the invention at 100 ppm catalyst. The rate of reaction is determined from the slope of this plot.

[0012] Figs. 2-5 are powder X-ray diffraction patterns for various zinc hexacyanocobaltate catalysts. The figures are described more fully below.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The double metal cyanide (DMC) catalysts of the invention generally resemble the catalysts known in the art, but contain a relatively low level of the metal salt. The catalysts of the invention are the reaction products of a water-soluble metal salt and a water-soluble metal cyanide salt. The water-soluble metal salt preferably has the general formula $M(X)_n$ in which M is selected from the group consisting of Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II), and Cr(III). More preferably, M is selected from the group consisting of Zn(II), Fe(II), Co(II), and Ni(II). In the formula, X is preferably an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate, and nitrate. The value of n is from 1 to 3 and satisfies the valency state of M. Examples of suitable metal salts include, but are not limited to, zinc chloride, zinc bromide, zinc acetate, zinc acetonylacetate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) formate, nickel(II) nitrate, and the like, and mixtures thereof. Zinc halides are preferred.

[0014] The water-soluble metal cyanide salts used to make the double metal cyanide compounds useful in the invention preferably have the general formula $(Y)_aM'(CN)_b(A)_c$ in which M' is selected from the group consisting of Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn (II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV), and V(V). More preferably, M' is selected from the group consisting of Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III), and Ni(II). The water-soluble metal cyanide salt can contain one or more of these metals. In the formula, Y is an alkali metal ion or alkaline earth metal ion. A is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate, and nitrate. Both a and b are integers greater than or equal to 1; the sum of the charges of a, b, and c balances the charge of M'. Suitable water-soluble metal cyanide salts include, but are not limited to, potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III), lithium hexacyanoiridate(III), and the like.

[0015] Examples of double metal cyanide compounds that can be used in the invention include, for example, zinc hexacyanocobaltate(III), zinc hexacyanoferrate (III), zinc hexacyanoferrate(II), nickel(II) hexacyanoferrate(II), cobalt(II) hexacyanocobaltate(III), and the like. Further examples of suitable double metal cyanide compounds are listed in U.S. Pat. No. 5,158,922.

[0016] The catalysts of the invention are prepared in the presence of a complexing agent added either during preparation or immediately following precipitation of the catalyst. As is explained elsewhere in this application, the manner in which the complexing agent is introduced

into the DMC complex can be extremely important. Usually, an excess amount of the complexing agent is used.

[0017] The complexing agent is an organic complexing agent which is a water-soluble aliphatic alcohol, suitable selected from the group consisting of ethanol; isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, and tert-butyl alcohol. Tert-butyl alcohol is most preferred.

[0018] The conventional method of preparing DMC compounds useful for epoxide polymerization is fully described in many references, including U.S. Patent Nos. 5,158,922, 4,843,054, 4,477,589, 3,427,335, 3,427,334, 3,427,256, 3,278,457, and 3,941,849, and Japanese Pat. Appl. Kokai No. 4-145123.

[0019] The catalysts of the invention differ from DMC catalysts known in the art in that those of the invention contain a relatively small proportion of the metal salt. Catalysts of the invention contain some metal salt, but in an amount less than 0,1 mole of metal salt per mole of DMC compound.

[0020] DMC complexes that contain no metal salt are inactive as epoxide polymerization catalysts. Thus, it is necessary to leave some metal salt in the catalyst during preparation. Excessive washing of the catalyst with water can deactivate DMC catalysts by removing all of the metal salt component, even if an excess of the metal salt is used to prepare the catalyst. DMC catalysts made by conventional methods with a large excess of metal salt contain more than 0.2, typically more than 0.5, moles of metal salt per mole of DMC compound.

[0021] The catalysts of the invention are substantially crystalline. Powder X-ray diffraction analysis shows that these catalysts have predominantly sharp lines, which indicates a relatively high degree of crystallinity (see Figs. 2 and 3). Interestingly, zinc hexacyanocobaltate dodecahydrate, which is prepared in the absence of a complexing agent, is also highly crystalline by X-ray analysis (see Fig. 4), but has no activity for polymerizing epoxides.

[0022] Earlier, we prepared highly active DMC catalysts that were substantially amorphous by X-ray diffraction analysis (see Fig. 5; see also EP-A-0654302). These catalysts had much greater activity than DMC catalysts previously known in the art. Catalysts that polymerize propylene oxide at rates greater than about 3 g PO/min. at 100 ppm of catalyst at 105°C (based on the weight of finished polyether) were obtained. Catalysts having both a high degree of crystallinity <u>and</u> high activity were not known.

[0023] We surprisingly found that catalysts prepared under conditions effective to leave a small proportion of metal halide in the catalysts are highly crystalline and can polymerize propylene oxide at a rate greater than about 3 g PO/min. at 100 ppm of catalyst at 105°C (based on the weight of finished polyether). For example, zinc hexacyanocobaltate catalysts prepared using the methods of the invention contained, by elemental analysis (chloride content), about 0.07 to 0.18 moles of zinc chloride per mole of zinc hexacyanocobaltate. The catalysts exhibit substantially crystalline powder X-ray diffraction patterns with signals present at about 6.1, 5.9, 5.1, 4.2, 3.8, 3.6, 2.5, and 2.3 (d-spacing, angstroms). Figs. 2 and 3 show powder X-ray diffraction patterns for catalysts of the invention.

[0024] In addition to their high activities, the catalysts of the invention give polyether polyol products having an exceptionally low level of unsaturation. The value of low-unsaturation polyols for making polyurethanes with excellent physical properties is well documented. Polyether polyols having unsaturations less than about 0.004 meq/g can be made using the catalysts of the invention.

[0025] The invention includes methods for making the highly active DMC complex catalysts. Generally, the methods used to make the catalysts of the invention resemble the methods known for making the highly active, substantially amorphous catalysts described in EP-A-0654302 and in US-A-5712216 In these methods, a substantially amorphous DMC catalyst is prepared either by: (1) intimately combining and reacting aqueous solutions of metal salt and metal cyanide salt in the presence of an organic complexing agent, usually with homogenization, high-shear, or impingement mixing of the reactants; or (2) reacting aqueous solutions of the metal salt and metal cyanide salt in the presence of the organic complexing agent, wherein one or both of the reactant solutions contains the complexing agent. When the second method is used (organic complexing agent present before reaction of metal salt and metal cyanide salt), intimate combination of the reactants is not required to obtain a substantially amorphous catalyst.

[0026] The methods of the invention, which vary these approaches somewhat, surprisingly give substantially crystalline DMC catalysts. The methods of the invention give catalysts that contain a relatively small proportion of metal salt compared with the substantially amorphous catalysts described in preceding paragraph.

[0027] One way to make a catalyst of the invention is to follow the procedures used to make a substantially amorphous catalyst, but to use less than a large excess of the metal salt in making the catalyst (see Example 3 and Fig. 3). Previous methods used a large excess of the metal salt. In this method of the invention, the metal salt is used in excess, but the excess amount is less than a 100% stoichiometric excess relative to the amount of metal cyanide salt. The resulting catalyst contains less than about 0.1 mole of the metal salt per mole of DMC compound in the catalyst. (Previous catalysts contained at least about 0.5 moles of the metal salt per mole of DMC compound in the catalyst.)

[0028] Another way to make a catalyst of the invention is to follow the procedures used to make a substantially amorphous catalyst, but to modify the washing routine (see Examples 1-2 and Fig. 2). In this method, aqueous solutions of the metal salt and metal cyanide salt are first reacted in the presence of an organic complexing

agent. As in the case of making substantially amorphous catalysts, the reactants are either intimately combined, or the organic complexing agent is present initially in one or both of the reactant solutions. The metal salt is used in an excess amount compared to the amount of metal cyanide salt, and the excess can be large or small. Unlike prior methods, this method washes the catalyst precipitate with a mixture of water and an organic complexing agent in a manner effective to produce a highly active DMC complex catalyst that contains less than about 0.1 mole of the metal salt per mole of DMC compound in the catalyst.

[0029] The amount and kind of washing needed to achieve less than about 0.1 mole of residual metal salt per mole of DMC compound in the catalyst depend on many factors, including which complexing agent is used, the relative amounts of water and organic complexing agent in the wash solutions, the number of washes, the volume of wash solution per gram of catalyst, the separation method used (i.e., filtration or centrifugation), and other factors. With routine experimentation, a skilled person can select conditions to make a catalyst of the invention that best suits her needs. The effectiveness of the washing routine can be gauged by measuring the chlorine and metals contents of the catalyst, and by inspecting the powder X-ray diffraction pattern exhibited by the catalyst.

[0030] The invention includes a process for making an epoxide polymer. This process comprises polymerizing an epoxide in the presence of a double metal cyanide catalyst composition of the invention. Preferred epoxides are ethylene oxide, propylene oxide, butene oxides, styrene oxide, and the like, and mixtures thereof. The process can be used to make random or block copolymers. The epoxide polymer is preferably a polyether polyol made by polymerizing an epoxide in the presence of a hydroxyl group-containing initiator.

[0031] Other monomers that will copolymerize with an epoxide in the presence of a DMC compound can be included in the process of the invention to make other types of epoxide polymers. Any of the copolymers known in the art made using conventional DMC catalysts can be made with the catalysts of the invention. For example, epoxides copolymerize with oxetanes (as taught in U.S. Pat. Nos. 3,278,457 and 3,404,109) to give polyethers, or with anhydrides (as taught in U.S. Pat. Nos. 5,145,883 and 3,538,043) to give polyester or polyetherester polyols. The preparation of polyether, polyester, and polyetherester polyols using double metal cyanide catalysts is fully described, for example, in U. S. Pat. Nos. 5,223,583, 5,145,883, 4,472,560, 3,941,849, 3,900,518, 3,538,043, 3,404,109, 3,278,458, 3,278,457, and in J.L. Schuchardt and S.D. Harper, SPI Proceedings, 32nd Annual Polyurethane Tech./Market. Conf. (1989) 360.

[0032] The DMC catalysts of the invention are highly active compared to conventional DMC catalysts. A consequence of higher polymerization rates is that polyol producers can use less of the relatively expensive DMC catalyst and save money. More active catalysts also permit the producer to reduce batch times and increase productivity. In addition, the catalysts of the invention are often active enough to allow their use at very low concentrations, such as 25 ppm or less. At such low concentrations, the catalyst can often be left in the polyether polyol without an adverse effect on product quality. The ability to leave catalysts in the polyol is an important advantage because commercial polyols currently require a catalyst removal step.

[0033] Polyether polyols prepared using the catalysts of the invention have exceptionally low unsaturations, consistently less than about 0.007 meq/g. Preferred polyols of the invention have unsaturations less than about 0.006 meq/g, and more preferably less than about 0.005 meq/g. The reduced unsaturation compared with polyols made with conventional DMC catalysts offers advantages for polyurethanes made with the polyols of the invention.

[0034] Polyether polyols made with the catalysts of the invention preferably have average hydroxyl functionalities from about 2 to 8, more preferably from about 2 to 6, and most preferably from about 2 to 3. The polyols preferably have number average molecular weights within the range of about 500 to about 50,000. A more preferred range is from about 1,000 to about 12,000; most preferred is the range from about 2,000 to about 8,000.

[0035] The following examples illustrate the invention.

Reference EXAMPLE 1

Preparation of a Zinc Hexacyanocobaltate/tert-Butyl Alcohol Complex Containing Less Than 0.2 moles of $ZnCl_2$ per mole of $Zn_3[Co(CN)_6]_2$

[0036] In this example, a 306% stoichiometric excess of zinc chloride is used to make the catalyst, but the washing routine reduces the amount of zinc chloride remaining to less than 0.2 moles per mole of zinc hexacyanocobaltate present in the catalyst.

[0037] Potassium hexacyanocobaltate (4 g) is dissolved in water (75 mL) to make Solution 1. Zinc chloride (10 g) is dissolved in distilled water (15 mL) to make Solution 2. Solution 3 contains tert-butyl alcohol (50 mL) and distilled water (150 mL).

[0038] Solution 1 is combined with Solution 3. The aqueous zinc chloride solution (Solution 2) is then added slowly while homogenizing the reactant mixture. After zinc chloride addition is complete, the mixture is homogenized for another 20 min.

[0039] The resulting solid catalyst is isolated by filtration (5 micron filter) at 40 psi. The wet solids are combined with tert-butyl alcohol (50 mL) and distilled water (50 mL), and the mixture is homogenized for 20 min. The catalyst is filtered as previously described. The wet solids are combined with tert-butyl alcohol (70 mL) and

distilled water (30 mL), the mixture is homogenized for 20 min., and the solids are isolated. Finally, the solids are combined with neat tert-butyl alcohol (100 mL), homogenized, and isolated. The solids are then dried in a vacuum oven at 50-60°C, 30 in. (Hg) for 4-5 h.

[0040] The catalyst polymerizes propylene oxide at a rate of 11.1 g/min (100 ppm catalyst, 105°C, as described in Example 4). Elemental analysis of the catalyst indicates 1.4 wt.% chloride content (0.14 moles of $ZnCl_2$ per mole of $Zn_3[Co(CN)_6]_2$). Powder X-ray diffraction analysis of the catalyst shows a substantially crystalline material that exhibits signals at about: 6.1, 5.9, 5.1, 4.2, 3.8, 3.6, 2.5, and 2.3 (d-spacing, angstroms) (see Fig. 2). A polyether triol made using the catalyst (see Example 5 for procedure) has an unsaturation of 0.0043 meq/g and a hydroxyl number of 30 mg KOH/g.

EXAMPLE 2

Preparation of a Zinc Hexacyanocobaltate/tert-Butyl Alcohol Complex Containing Less Than 0.1 moles of $ZnCl_2$ per mole of $Zn_3[Co(CN)_6]_2$

[0041] This example illustrates the preparation of a DMC catalyst by using only a 63% stoichiometric excess of the metal salt to prepare the catalyst.

[0042] A one-liter round-bottom flask equipped with mechanical stirrer, pressure-equalizing addition funnel, and thermometer is charged with potassium hexacyanocobaltate (5.0 g), tert-butyl alcohol (95 g), and distilled water (445 g). The mixture is stirred until all of the metal cyanide salt dissolves. The solution is warmed to 25°C. A solution of zinc chloride (5 g) in water (5 g) is added over 1 min. to the stirred reaction mixture. Stirring continues for another 30 min. at 25°C.

[0043] The resulting white suspension is filtered through a pressure filter at 30 psig. The solids are resuspended with vigorous stirring in a solution of tert-butyl alcohol (68 g) and water (38 g), which is a 70:30 (by volume) solution. After all of the solids are completely suspended in the wash mixture, stirring continues for an additional 30 min. The solids are again isolated by pressure filtration, and are resuspended in tert-butyl alcohol (99.5%) (98 g, 125 mL). After all of the solids are completely suspended in the wash mixture, stirring continues for an additional 30 min. The solids are isolated and dried in a vacuum oven at 45°C, 30 in. (Hg) for 18 h.

[0044] The catalyst polymerizes propylene oxide at a rate of 10.9 g/min (100 ppm catalyst, 105°C, as described in Example 3). Elemental analysis of the catalyst indicates 0.7 wt.% chloride content (0.07 moles of $ZnCl_2$ per mole of $Zn_3[Co(CN)_6]_2$). Powder X-ray diffraction analysis of the catalyst (see Fig. 3) shows a substantially crystalline material that exhibits signals at about: 6.1, 5.9, 5.1, 4.2, 3.8, 3.6, 3.1, 2.5, 2.3, and 2.1 (d-spacing, angstroms). A polyether triol made using the catalyst (see Example 4 for procedure) has an unsaturation of 0.0026 meq/g and a hydroxyl number of 29.8 mg KOH/g.

EXAMPLE 3

Epoxide Polymerizations: Rate Experiments--General Procedure

[0045] A one-liter stirred reactor is charged with polyoxypropylene triol (700 mol. wt.) starter (70 g) and zinc hexacyanocobaltate catalyst (0.057 g, 100 ppm level in finished polyol). The mixture is stirred and heated to 105°C, and is stripped under vacuum to remove traces of water from the triol starter. The reactor pressure is adjusted to a vacuum of about 30 in. (Hg), and propylene oxide (10-11 g) is added in one portion. The reactor pressure is then monitored carefully. Additional propylene oxide is not added until an accelerated pressure drop occurs in the reactor; the pressure drop is evidence that the catalyst has become activated. When catalyst activation is verified, the remaining propylene oxide (490 g) is added gradually to keep the reactor pressure at about 10 psig. After propylene oxide addition is complete, the mixture is held at 105°C until a constant pressure is observed. Residual unreacted monomer is then stripped under vacuum from the polyol product, and the polyol is cooled and recovered.

[0046] To determine reaction rate, a plot of PO consumption (g) vs. reaction time (min) is prepared (see Fig. 1). The slope of the curve at its steepest point is measured to find the reaction rate in grams of PO converted per minute. The intersection of this line and a horizontal line extended from the baseline of the curve is taken as the induction time (in minutes) required for the catalyst to become active.

[0047] When this procedure is used to measure propylene oxide polymerization rates, the catalysts of the invention typically polymerize PO at rates in excess of about 10 g/min at 100 ppm catalyst at 105°C (see Fig. 1). In contrast, a catalyst made by the procedure of U. S. Pat. No. 5,158,922 polymerizes PO at a rate of about 2 g/min. at 100 ppm catalyst at 105°C.

EXAMPLE 4

Polyether Polyol Synthesis

[0048] A two-gallon stirred reactor is charged with polyoxypropylene triol (700 mol. wt.) starter (685 g) and zinc hexacyanocobaltate catalyst (1.63 g). The mixture is stirred and heated to 105°C, and is stripped under vacuum to remove traces of water from the triol starter. Propylene oxide (102 g) is fed to the reactor, initially under a vacuum of about 30 in. (Hg), and the reactor pressure is monitored carefully. Additional propylene oxide is not added until an accelerated pressure drop occurs in the reactor; the pressure drop is evidence that the catalyst has become activated. When catalyst activation is verified, the remaining propylene oxide (5713 g) is added gradually over about 2 h while maintaining a reactor pressure less than 40 psi. After propylene oxide

addition is complete, the mixture is held at 105°C until a constant pressure is observed. Residual unreacted monomer is then stripped under vacuum from the polyol product. The hot polyol product is filtered at 100°C through a filter cartridge (0.45 to 1.2 microns) attached to the bottom of the reactor to remove the catalyst.

Claims

1. A double metal cyanide (DMC) complex crystalline catalyst which comprises a DMC compound, an organic complexing agent which is a water-soluble aliphatic alcohol, and a metal salt, wherein the catalyst contains less than 0.1 mole of the metal salt per mole of DMC compound.

2. A catalyst as claimed in claim 1 **characterised in that** the DMC compound is a zinc hexacyanocobaltate and the metal salt is a zinc halide.

3. A catalyst as claimed in claim 1 or 2 **characterised in that** the organic complexing agent is tert-butyl alcohol.

4. A catalyst as claimed in any one of the preceding claims **characterised in that** it is substantially crystalline and has powder X-ray diffraction signals at about 6.1, 5.9, 5.1, 4.2, 3.8, 3.6, 2.5, and 2.3 (d-spacing, angstroms).

5. A catalyst as claimed in any one of claims 1 to 4 and having a powder X-ray diffraction pattern substantially as shown in Fig. 2.

6. A catalyst as claimed in any one of the preceding claims **characterised in that** it is effective to polymerize propylene oxide at a rate in excess of 3 g PO/min at 100 ppm of catalyst, based on the weight of finished polyether, at 105°C.

7. A catalyst as claimed in any one of the preceding claims **characterised in that** it is capable of producing a polyether polyol having an unsaturation less than 0.005 meq/g.

8. A method of making a highly active DMC complex crystalline catalyst according to claim 1, said method comprising reacting aqueous solutions of a metal salt and a metal cyanide salt in the presence of an organic complexing agent, wherein the metal salt is used in an excess amount less than a 100% stoichiometric excess relative to the amount of metal cyanide salt, and the resulting catalyst contains less than 0.1 mole of the metal salt per mole of DMC compound in the catalyst.

9. A method of making a highly active DMC complex crystalline catalyst according to claim 1, said method comprising:

   (a) reacting aqueous solutions of a metal salt and a metal cyanide salt in the presence of an organic complexing agent to produce a catalyst precipitate, said metal salt being used in excess compared with the amount of metal cyanide salt used; and
   (b) washing the catalyst precipitate with a mixture of water and organic complexing agent in a manner effective to produce a highly active DMC complex catalyst that contains less than 0.1 mole of the metal salt per mole of DMC compound in the catalyst.

10. A method as claimed in claim 8 or claim 9 **characterised in that** the DMC catalyst is a zinc hexacyanocobaltate.

11. A method as claimed in claim 8, claim 9 or claim 10 **characterised in that** the organic complexing agent is tert-butyl alcohol.

12. A method as claimed in any one of claims 8 to 11 **characterised in that** the DMC catalyst is substantially crystalline and has powder X-ray diffraction signals at about 6.1, 5.9, 5.1, 4.2, 3.8, 3.6, 2.5, and 2.3 (d-spacing, angstroms).

13. A method of preparing an epoxide polymer, said method comprising polymerizing an epoxide in the presence of a catalyst as claimed in any one of claims 1 to 7 or obtained by a method as claimed in any one of claims 8 to 12.

Patentansprüche

1. Kristalliner Doppelmetallcyanid(DMC)komplex-Katalysator, umfassend eine DMC-Verbindung, einen organischen Komplexbildner, der ein wasserlöslicher aliphatischer Alkohol ist, und ein Metallsalz, wobei der Katalysator weniger als 0,1 mol des Metallsalzes pro mol der DMC-Verbindung enthält.

2. Katalysator gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die DMC-Verbindung ein Zinkhexacyanocobaltat ist, und das Metallsalz ein Zinkhalogenid ist.

3. Katalysator gemäß den Ansprüchen 1 oder 2, **dadurch gekennzeichnet, dass** der organische Komplexbildner tert-Butylalkohol ist.

4. Katalysator gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** er im Wesentlichen kristallin ist und Pulver-Rönt-

genbeugungssignale bei etwa 6,1, 5,9, 5,1, 4,2, 3,8, 3,6, 2,5 und 2,3 (d-Abstand, Å) hat.

5. Katalysator gemäß irgendeinem der Ansprüche 1 bis 4, der ein Pulver-Röntgenbeugungsmuster aufweist, wie es im Wesentlichen in Fig. 2 gezeigt wird.

6. Katalysator gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** er wirksam ist, um Propylenoxid mit einer Rate von mehr als 3 g PO/min bei 100 ppm Katalysator, bezogen auf das Gewicht des fertigen Polyethers, bei 105 °C zu polymerisieren.

7. Katalysator gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** er befähigt ist, ein Polyetherpolyol herzustellen, das eine Nichtsättigung von weniger als 0,005 Milliäquivalenten/g aufweist.

8. Verfahren zur Herstellung eines hochaktiven, kristallinen DMC-Komplex-Katalysators gemäß Anspruch 1, wobei das Verfahren die Umsetzung wässriger Lösungen eines Metallsalzes und eines Metallcyanidsalzes in Gegenwart eines organischen Komplexbildners umfasst, wobei das Metallsalz in einer überschüssigen Menge verwendet wird, die geringer ist als ein 100%iger stöchiometrischer Überschuss, bezogen auf die Menge des Metallcyanidsalzes, und der sich ergebende Katalysator weniger als 0,1 mol des Metallsalzes pro mol der DMC-Verbindung in dem Katalysator enthält.

9. Verfahren zur Herstellung eines hochaktiven, kristallinen DMC-Komplex-Katalysators gemäß Anspruch 1, wobei das Verfahren folgendes umfasst:

(a) die Umsetzung wässriger Lösungen eines Metallsalzes und eines Metallcyanidsalzes in Gegenwart eines organischen Komplexbildners, um einen Katalysator-Niederschlag zu bilden, wobei das Metallsalz in einem Überschuss, verglichen mit der Menge des verwendeten Metallcyanidsalzes, verwendet wird;
(b) das Waschen des Katalysator-Niederschlags mit einer Mischung von Wasser und organischem Komplexbildner auf eine Weise, die wirksam ist, um einen hochaktiven DMC-Komplex-Katalysator herzustellen, der weniger als 0,1 mol des Metallsalzes pro mol DMC-Verbindung in dem Katalysator enthält.

10. Verfahren gemäß den Ansprüchen 8 oder 9, **dadurch gekennzeichnet, dass** der DMC-Katalysator ein Zinkhexacyanocobaltat ist.

11. Verfahren gemäß den Ansprüchen 8, 9 oder 10, **dadurch gekennzeichnet, dass** der organische Komplexbildner tert-Butylalkohol ist.

12. Verfahren gemäß irgendeinem der Ansprüche 8 bis 11, **dadurch gekennzeichnet, dass** der DMC-Katalysator im Wesentlichen kristallin ist und Pulver-Röntgenbeugungssignale bei etwa 6,1, 5,9, 5,1, 4,2, 3,8, 3,6, 2,5 und 2,3 (d-Abstand, Å) hat.

13. Verfahren zur Herstellung eines Epoxid-Polymers, wobei das Verfahren die Polymerisation eines Epoxids in Gegenwart eines Katalysators umfasst, wie er gemäß irgendeinem der Ansprüche 1 bis 7 beansprucht wird oder durch ein Verfahren gemäß irgendeinem der Ansprüche 8 bis 12 erhalten wird.

Revendications

1. Catalyseur cristallin à base de complexe de cyanure métallique double (DMC) qui comprend un composé DMC, un agent complexant organique qui est un alcool aliphatique hydrosoluble, et un sel métallique, où le catalyseur contient moins de 0,1 mol de sel métallique par mole de composé DMC.

2. Catalyseur selon la revendication 1, **caractérisé en ce que** le composé DMC est un hexacyanocobaltate de zinc et le sel métallique est un halogénure de zinc.

3. Catalyseur selon la revendication 1 ou 2, **caractérisé en ce que** l'agent complexant organique est l'alcool tert-butylique.

4. Catalyseur selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**il est sensiblement cristallin et a des signaux de diffraction des rayons X de poudre à environ 6,1, 5,9, 5,1, 4,2, 3,8, 3,6, 2,5 et 2,3 (distance d, angströms).

5. Catalyseur selon l'une quelconque des revendications 1 à 4 et ayant un diagramme de diffraction des rayons X de poudre sensiblement tel qu'indiqué sur la figure 2.

6. Catalyseur selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**il est efficace pour polymériser l'oxyde de propylène à un débit dépassant 3 g de OP/min à 100 ppm de catalyseur, par rapport à la masse de polyéther achevé, à 105°C.

7. Catalyseur selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**il est capable de produire un polyétherpolyol ayant une insaturation inférieure à 0,005 meq/g.

8. Procédé de production d'un catalyseur cristallin à

base de complexe de DMC hautement actif selon la revendication 1, ledit procédé comprenant la réaction de solutions aqueuses d'un sel métallique et d'un sel cyanure métallique en présence d'un agent complexant organique, où le sel métallique est utilisé en une quantité excessive inférieure à un excès stoechiométrique de 100 % par rapport à la quantité de sel cyanure métallique, et le catalyseur résultant contient moins de 0,1 mol de sel métallique par mole de composé DMC dans le catalyseur.

9. Procédé de production d'un catalyseur cristallin à base de complexe de DMC hautement actif selon la revendication 1, ledit procédé comprenant :

(a) la réaction de solutions aqueuses d'un sel métallique et d'un sel cyanure métallique en présence d'un agent complexant organique pour produire un précipité de catalyseur, ledit sel métallique étant utilisé en excès par rapport à la quantité de sel cyanure métallique utilisée ; et

(b) le lavage du précipité de catalyseur avec un mélange d'eau et d'agent complexant organique d'une manière efficace pour produire un catalyseur à base de complexe de DMC hautement actif qui contient moins de 0,1 mol de sel métallique par mole de composé DMC dans le catalyseur.

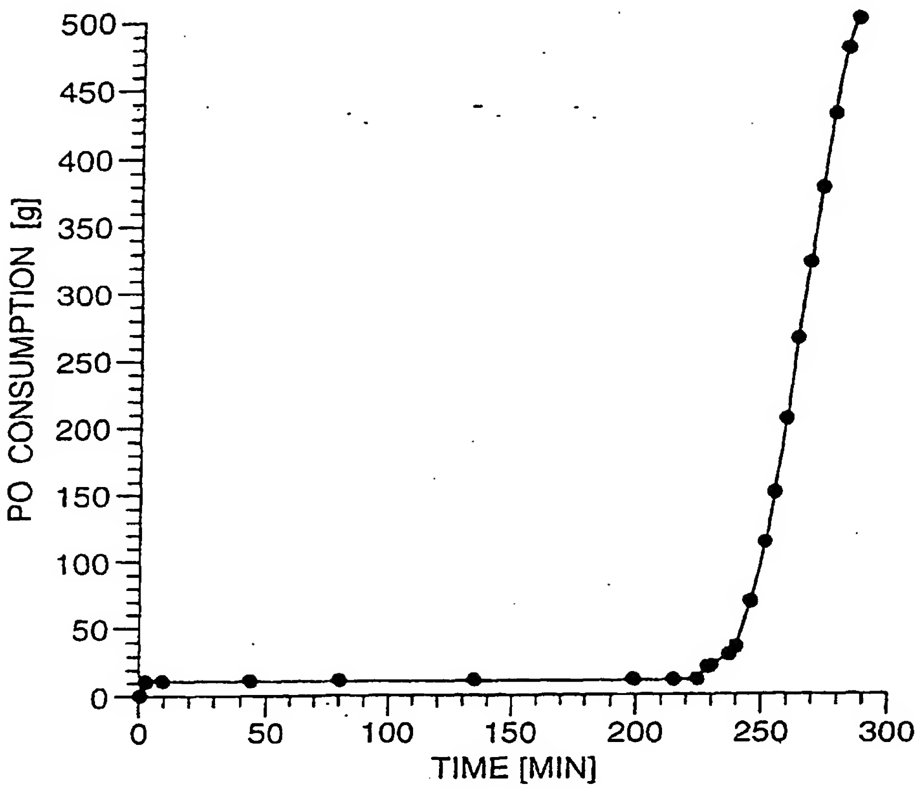
10. Procédé selon la revendication 8 ou la revendication 9, **caractérisé en ce que** le catalyseur DMC est un hexacyanocobaltate de zinc.

11. Procédé selon la revendication 8, la revendication 9 ou la revendication 10, **caractérisé en ce que** l'agent complexant organique est l'alcool tert-butylique.

12. Procédé selon l'une quelconque des revendications 8 à 11, **caractérisé en ce que** le catalyseur DMC est sensiblement cristallin et a des signaux de diffraction des rayons X de poudre à environ 6,1, 5,9, 5,1, 4,2, 3,8, 3,6, 2,5 et 2,3 (distance d, angströms).

13. Procédé de préparation d'un polymère d'époxyde, ledit procédé comprenant la polymérisation d'un époxyde en présence d'un catalyseur selon l'une quelconque des revendications 1 à 7 ou obtenu par un procédé selon l'une quelconque des revendications 8 à 12.

Fig.1.



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150
200
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TIME [MIN]

Fig.2.

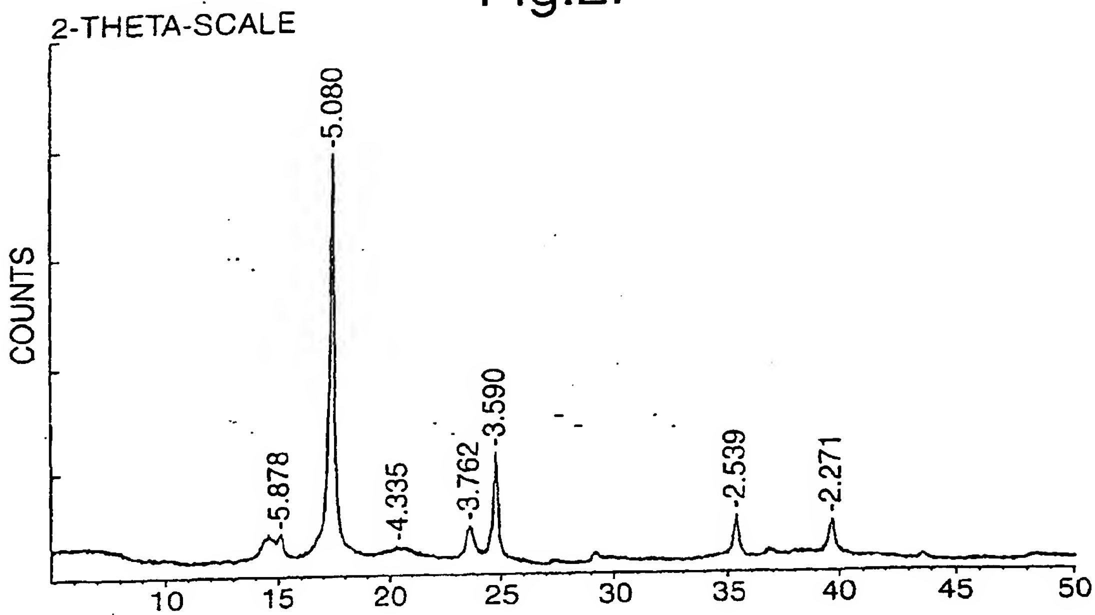
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Fig.3.

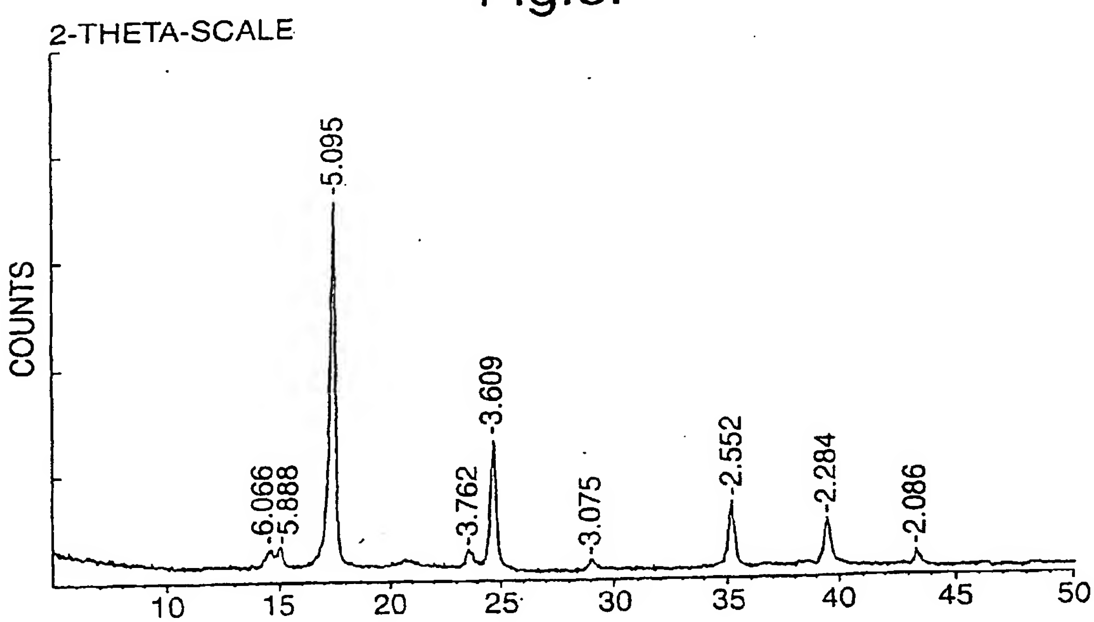
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Fig.4.

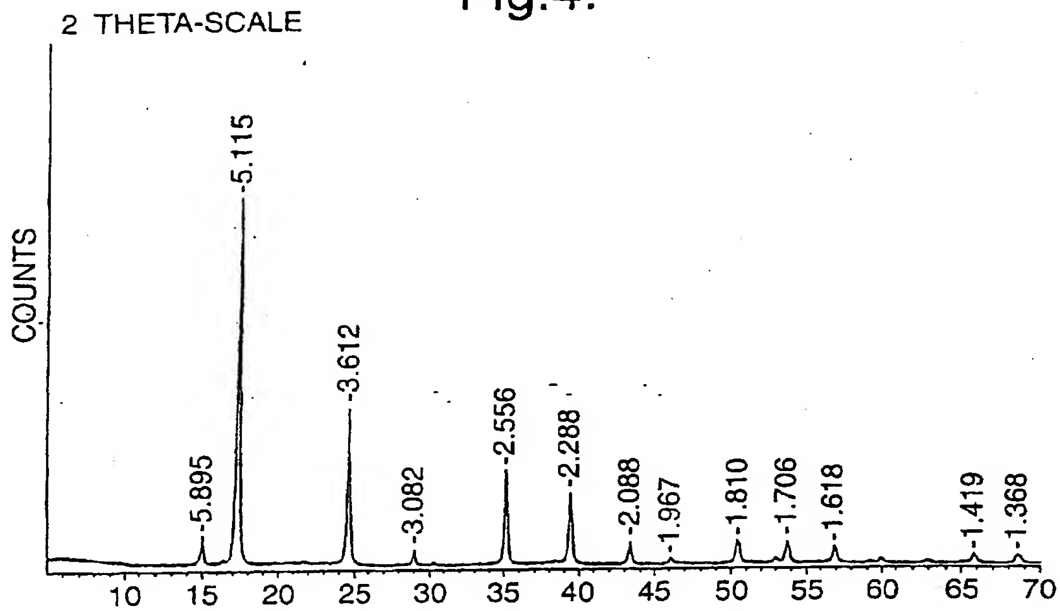
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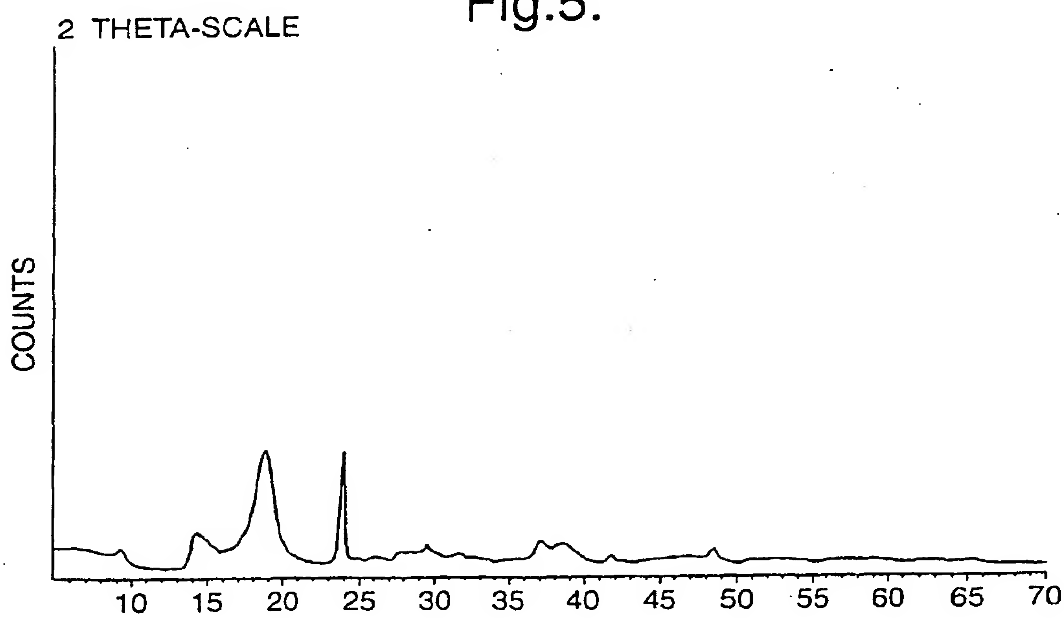
Fig.5.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